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RESEARCH MEMORANDUM

DEVELOPMENT OF METAL-BONDING ADHESIVES WITH

IMPROVED HEAT-RESISTANT PROPERTIES

By John M. Black and R. F. Blomquist

Forest Products Laboratory

NATIONAL ADVISORY COMMITTEE
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SUMMARY

Results are reported of current studies at the Forest Products Laboratory to develop a metal-bonding adhesive with greater resistance to temperatures up to 600° F that is easier to use than present ones. Most promising is a formulation of phenol and epoxy resins modified with hexamethylenetetramine and supplied for use as a dry tape supported on a glass-mat base.

INTRODUCTION

The present paper is a report on the development of metal-bonding adhesives with improved heat-resistant properties undertaken at the Forest Products Laboratory under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics. The work described in this report is a continuation of the work on adhesive formulations based on phenol resins and epoxy resins reported in reference 1. In reference 1 an adhesive designated as FPL-710 was described that developed promising shear strength when tested at elevated temperatures up to 600° F and also possessed good resistance to aging at temperatures as high as 450° F. The principal limitations of adhesive FPL-710 were that it was somewhat brittle, it possessed marginal bend and fatigue strength and variable performance at 600° F, and the optimum film thickness for bonding (0.002 inch) was too thin for practical use in aircraft.

The objectives of the investigation were to improve the performance of adhesive FPL-710 at 450° to 600° F and still maintain adequate shear strength at -70° F, to reduce brittleness, and to improve resistance to bending, peel, and fatigue. It was also planned to investigate the performance of FPL-710 and subsequent improved formulations for the bonding of stainless steel and titanium and to investigate their possible use as laminating resins for glass fabrics for service at high temperature. In addition, work was to be undertaken to make these adhesives as simple as possible to use in the production of bonded parts.

EXPERIMENTAL PROCEDURE

Changes in FPL-710 Adhesive

The preparation and recommended application and bonding procedure for FPL-710 adhesive were reported in reference 1. The present investigation has resulted in one change in formulation, namely, in the amount of hexamethylenetetramine (hexa) included. The presently recommended formulation for the adhesive is 4 grams of hexa (instead of 6 grams), 100 grams of Bakelite BV 9700, and 20 grams of Epon resin 1007 dissolved in methyl ethyl ketone. The recommended cure of the adhesive has also been changed to 30 minutes at 320° F instead of 60 minutes at 280° F.

Test Methods and Test Results

Test specimens of 0.064-inch 24S-T3 clad aluminum alloy with a 0.5-inch lap joint, as described in reference 2, were used for evaluation of shear strength when made immediately at each of the test temperatures and after the various aging conditions.

Lap-shear specimens were loaded in self-alining grips at the rate of 300 pounds per 0.5 square inch per minute. Bending test specimens were loaded flatwise at the center as a simple beam with a 1.5-inch span at the rate of 200 pounds per minute as described in reference 2. The loading block was over the center of the bonded area.

Elevated test temperatures were controlled to within ±3° F of the desired temperature. In tests at elevated temperatures, a period of 3 to 5 minutes was required to heat the specimens from room temperature to the test temperature. In tests made at the elevated temperature and at -70° F the load was applied as soon as the specimen reached the desired temperature.

Preparation of Mat-Tape Adhesive

The mat-tape adhesive is prepared by dipping fiber-glass mat of 0.010-inch thickness in liquid FPL-710, allowing it to drain, then air-drying and precuring it at 180° F. The optimum amounts of impregnation and the recommended conditions of drying have not been fully established. Samples of such a tape adhesive aged for 12 months at room temperature have shown no loss in resultant lap-shear strength when compared with bonds made initially with the fresh tape.

Metal Cleaning

Unless otherwise noted, the aluminum surfaces were prepared for bonding by immersion for 5 to 10 minutes in a solution of sulfuric acid (10 grams) and sodium dichromate (1 gram) in 30 grams of water at 140° to 160° F, followed by a rinse in cold running water, another with hot water or steam, and air-drying.

RESULTS AND CONCLUSIONS

Strength Properties at 600° F

Efforts to improve the consistency of results with FPL-710 adhesive when tested immediately at 600° F were the center of considerable study during the year. It had been previously observed that shear strength at 600° F would frequently vary from 100 to more than 1,000 psi. In attempting to overcome this limitation, a study was made of many bonding variables and variations in the adhesive formulation of FPL-710. In the course of the investigation, bonding variables studied included the method of metal surface preparation, amount of spread, age of stock adhesive, age of thinned adhesive, degree of solvent removal, bonding pressure, precure, and curing conditions. Variations in adhesive formulation, such as the amount of hexa, ratio of phenol resin to epoxy resin, amount of water, amount of refluxing, amount and type of solvent, and use of different epoxy and different phenol resins, were also studied to determine their possible effect on the immediate strength of the adhesive bonds at 600° F. Results of some of the more significant studies are given below.

Effect of postcuring.- One fact was well established, namely, that lap joints bonded with FPL-710 and aged for 192 hours at 450° F consistently exceeded 1,000 psi in shear strength when tested immediately at 600° F. This, of course, suggested possible advantages in elevated-temperature postcuring of bonds cured initially under conventional conditions. Shear tests of aluminum lap joints at 600° F have shown that the strength of bonds given a postcure without pressure were significantly higher and more consistent than bonds tested at 600° F after initial cure only. Table 1 shows the effect of postcure on joint strength at 600° F and the variation in joint strength at this temperature of lap-shear specimens of 0.064-inch clad aluminum alloy bonded with FPL-710 adhesive.

Supported film adhesive.- From previous work it was also known that 0.5-inch lap joints of 0.032-inch clad aluminum alloy made with FPL-710 without postcuring were low in strength at 600° F (about 150 psi) when compared with similar bonds of 0.064-inch clad alloy (about 470 psi). No significant differences were noted in bond strengths on these two metal thicknesses tested at temperatures of 450° F or lower. In current work a similar effect of the thickness of the metal on the immediate strength of lap joints at 600° F was observed on bonds of stainless steel. Lap joints of 26-gage (0.016 inch) stainless steel had an average shear strength of 430 psi, while 16-gage (0.061 inch) stainless steel had an average shear strength of 800 psi at 600° F. This performance of lap joints of metals of different thickness when tested at 600° F indicated that, since joint strength is apparently closely related to the relative physical properties of the metal and the cured adhesive and to the resultant stress concentrations in the joints under test, the joint strength might be improved appreciably by the use of a supporting fabric in the adhesive bond.

In subsequent tests made on metal lap joints bonded with a tape adhesive composed of a woven glass-fiber cloth impregnated with liquid FPL-710, the immediate strength of joints at 600° F was materially improved.

Further investigation of various glass-fiber cloths and mats for carriers of the adhesives was undertaken, and the most promising material at the present time appears to be a glass-fiber mat with furfural binder that is approximately 0.010 inch thick (Owens-Corning Fiberglas mat S11Mol). The use of this mat impregnated with FPL-710 adhesive to form a dry tape adhesive has resulted in greater reproducibility and consistently stronger bonds when tested immediately at 600° F without postcuring when compared with joints made with the liquid adhesive and tested under the same conditions. The joints made with liquid adhesive, however, were higher in shear strength at 600° F after a postcure than joints made with the mat-tape adhesive. The mat-tape FPL-710 adhesive is also considered to be superior to the liquid adhesive in ease of application, which would be a distinct advantage in a production bonding process, and also develops bonds which are 0.008 to 0.010 inch thick as contrasted with a film thickness of about 0.002 inch obtained with the liquid adhesive.

A comparison of typical average results of tests of lap-shear specimens at -70° to 600° F bonded with FPL-710 adhesive applied by brush, spraying, and as the impregnated mat described above is shown in table 2. The minimum and maximum failing loads at 600° F are also given in parentheses in the last column.

Resistance to Aging at Elevated Temperatures

As can be seen from table 2, lap joints of clad aluminum alloy properly made with the liquid FPL-710 adhesive applied by brush or spray have shown a high degree of resistance to thermal degradation as indicated by the retention of joint strength at temperatures up to 600° F after aging for 192 hours at 450° F. Test specimens aged for 192 hours at 450° F and subsequently tested at temperatures from -70° to 600° F retained half or more of their initial strength at room temperature and had a strength exceeding 1,200 psi at each of the temperatures ranging from -70° to 600° F. A study of the performance of this adhesive when aged at temperatures above 450° F has shown that a considerable loss in strength in joints made with the standard FPL-710 formulation may occur when the temperature is increased to 550° F, as follows:

Heat-exposure conditions		Shear strength at 80° F, psi
Time, hr	Temperature, °F	
None	---	3,020
192	450	1,980
192	550	350

Effect of amount of hexamethylenetetramine.- Further study of the effect of adhesive composition revealed that the amount of hexa present influenced the resistance of the adhesive to aging for 192 hours at 550° F. A quantity of 5 percent based on the combined weight of phenol and epoxy resins (4 grams hexa, 100 grams BV 9700, 20 grams Epon 1007) appears to have the greatest resistance to aging for this period as shown in the following data, but further work is probably warranted to determine the optimum amount more accurately.

Amount of hexa, percent	Shear strength at 80° F after 192 lb at 550° F, psi
0	290
5	670
7.5	350

Effect of stabilizers.- The cause of the relatively low performance characteristics of adhesive FPL-710 to aging at 550° F as contrasted with the high performance at 450° F previously cited was investigated further. It was known that 24S-T3 clad aluminum alloy contains approximately 0.1 percent of copper and 0.7 percent of combined silicon and iron in the clad face of the alloy. The metals copper and iron, even in very small amounts, are also known to be effective catalysts for the oxidation and degradation of organic materials in many reactions (ref. 3) and could be promoting the thermal degradation of adhesive FPL-710 during the exposure for 200 hours at 550° F. It was then shown in tests of lap joints of brass bonded with FPL-710 and aged at 550° F for 200 hours that the adhesive was completely decomposed to a black char after this exposure. This was considered a further indication that the metal, and presumably the copper present in the brass, could have a significant effect on the performance and the resistance of the adhesive to thermal degradation under these conditions.

In other fields of research, as in hydrocarbon fuels, the deactivation of catalytic metals, particularly copper, has been accomplished by certain chelating agents as described by Watson and Tom (ref. 3). These chelating agents have also been used to retard the thermal breakdown in cellulose ester (ref. 4). The stability and structure of metal chelate compounds have been investigated by various authors (refs. 5 and 6). A study of the effect of several potential chelating agents as adhesive stabilizers in the present work revealed that the resistance of FPL-710 adhesive with 5 percent of hexa to aging for 200 hours at 550° F was improved in some cases. A quantity of 1 percent of FPL-710 adhesive based on the weight of the resin solids was employed and joints were tested at 80° F after aging 200 hours at 550° F. The adhesive also contained 5 percent of hexa. The following tabulation shows the results of these tests:

Stabilizer	Shear strength at 80° F, psi
None	670
8-Quinolinol	960
Salicylic acid	890
Salicylaldehyde	785
Acetyl acetone	985
Acetonyl acetone	965
Aluminum triacetonyl acetonate	960
Catechol	980
Gallic acid	820
o-Aminophenol	320
Ethylene diamine	835
Oxalic acid	120
Mucic acid	480
Tartaric acid	320
Copper citrate	480
Triethanolamine titanate	440

Several of the chelate stabilizers were particularly promising as agents for retarding the thermal degradation of the adhesive. The materials 8-Quinolinol, acetyl acetone, acetonyl acetone, aluminum triacetonyl acetonate, and catechol were most effective and resulted in a retention of 960- to 980-psi shear strength at room temperature after aging 200 hours at 550° F. These strength values after aging represent approximately 40 percent of the control strength at room temperature. Even greater resistance to thermal degradation may be made possible by further work to determine the optimum amounts of hexa and of chelating agent to be employed in the adhesive formulation.

Bonding of Titanium and Stainless Steel With FPL-710 Adhesive

A limited investigation was made of the liquid adhesive FPL-710 with 5 percent of hexa for bonding titanium and stainless steel, which are metals with better heat-resistant properties than clad aluminum alloy. This work consisted primarily of ascertaining the effect of various methods of preparing the surface for bonding on the strength properties of the bond and the resistance of these bonds to aging for 200 hours at 550° F. The results of lap-shear tests at room temperature in this study of metal-surface preparation after an initial cure of 30 minutes at 320° F are shown in the following tabulation:

Metal	Method of cleaning	Shear strength at room temperature, psi
Titanium RC-30, 1/2 hard, 0.032 in. thick	Sulfuric-acid - sodium-dichromate bath	825
Do------------	Nitric-acid - hydrofluoric-acid bath	2,020
Stainless steel, type 302, annealed, 26 gage	Sulfuric-acid - sodium-dichromate bath	1,840
Do------------	Abraded with emery cloth	2,235
Do------------	Wipe with lacquer thinner	1,740
Do------------	Metasilicate degrease	1,760
Do------------	Hydrochloric-acid - peroxide-formalin bath	2,680

Of these methods, the most effective method of preparing titanium for bonding was immersion in a bath consisting of 9 parts by volume of concentrated nitric acid, 1 part of 50 percent hydrofluoric acid, and 30 parts of water. The metal was immersed for 20 minutes at 120° F, then rinsed and dried. Stainless steel was cleaned most effectively with a solution of 50 parts by weight of concentrated hydrochloric acid, 2 parts of 30 percent hydrogen peroxide, 10 parts of formalin solution, and 45 parts of water maintained at a temperature of 140° to 150° F. The metal was immersed for a period of 10 minutes. Additional tests were made on similar joints of titanium and stainless steel cleaned by these more effective methods and results are compared with values obtained on joints of clad aluminum alloy prepared by the sulfuric-acid - sodium-dichromate process tested under similar conditions in table 3.

These data revealed several interesting phenomena. The bonds of FPL-710 adhesive on titanium showed practically no resistance to aging at 550° F and were almost completely charred after 192 hours of exposure. This loss in resistance to aging at 550° F may have been caused by the method of preparing the titanium surfaces for bonding, which employed a mixture of nitric and hydrofluoric acids, but further work is needed to explain this behavior of the adhesive more fully. The resistance of FPL-710 to aging at 550° F in bonds of stainless steel, on the other hand, was particularly good and exceeded that obtained on bonds of aluminum. The bonds of stainless steel were also outstanding in their performance at -70° F, where there was no appreciable loss in shear strength from that obtained in tests at room temperature.

These limited tests on the different metals have revealed that the type of metal, the method of preparation for bonding, and presumably the mechanical properties of the metal at various test conditions have a major effect on the performance of the adhesive in elevated-temperature exposures. A more extensive study of metal bonding along these lines is needed and may be very helpful in formulating adhesives with improved performance characteristics.

Other Phenol Resins

In the course of the study of variables affecting the performance of adhesive at 600° F, two additional phenolic resins, Durez 15956 and Durez 16227, were evaluated as replacements for the same amount of Bakelite BV 9700 in the liquid form of FPL-710 and appeared to be quite promising. When either of these phenol resins was employed with Epon resin 1007 without additional curing agents (adhesives FPL-856d and FPL-857f) applied by brushing, joint strength when tested immediately at 600° F was slightly higher than that obtained with FPL-710 and test results showed greater consistency in three separate series of tests than had been observed with FPL-710 in liquid form. These resins were also promising because of the resultant improved flow properties in the mixed adhesive in the uncured state over those made with Bakelite BV 9700, presently employed in FPL-710. This greater degree of flow resulted in a film from which it was apparently less difficult to remove solvent and air before curing. Moreover flow was improved at a lower pressure during bonding, without reducing the subsequent heat resistance of the cured bond.

The bond strength at room temperature of the adhesive employing the Durez resin, however, was lower than that of FPL-710, and bonds also appeared to be more brittle than those made with FPL-710. The over-all properties of the adhesive formulations with the Durez resins were, therefore, probably no more promising than the adhesive FPL-710.

Reduction of Brittleness

A number of studies were directed toward reducing apparent brittleness of the cured adhesive bonds of liquid FPL-710 in lap joints of 24S-T3 clad aluminum alloy by incorporating rubbers or other elastic materials into the phenol-epoxy resin formulations. In these studies the brittle properties and apparent resistance to peel were determined qualitatively in lap-shear test specimens by observing the behavior of the bonds in 0.064-inch aluminum when the panels were handled, cut into individual specimens, and tested, as well as by breaking open lap joints of 0.032-inch clad aluminum by hand and applying the bend test described in reference 2. No peel tests were made on sandwich-type specimens.

Investigations to reduce the brittleness and improve peel properties of FPL-710 adhesive by variations in bonding procedures and variations in formulations have not yet been entirely successful. A significant improvement in peel resistance was obtained only when synthetic rubber was included in the formulation. When the rubber was incorporated in solution form, however, the adhesive mixture usually became incompatible in solution, and appreciable bond strength was lost at elevated temperatures. One experimental adhesive composed of phenol resin (200 parts Bakelite BV 9700), epoxy resin (15 parts Epon 1001), and buna N rubber (50 parts Hycar OR-15) was considered a promising formulation because of its compatibility and generally good strength properties at elevated temperatures. This adhesive was prepared by milling the components together on a rubber mill with considerable difficulty. This technique resulted in satisfactory compatibility in solution in methyl ethyl ketone and in strength at elevated temperatures, but in no apparent increase in peel resistance over FPL-710. Further study of adhesive formulations of this type employing greater amounts of rubber and prepared by a milling process should be considered as a possible approach to improved peel resistance.

Sandwich Construction

In a few limited tests recently the use of FPL-710 mat-type adhesive to bond metal faces to heat-resistant honeycomb cores for a sandwich was particularly promising. The use of the impregnated mat permitted the addition of sufficient adhesive to the face of the sandwich to form fillets on the edges of the honeycomb core, and also appeared to increase the resistance of the faces to peeling. In a few individual shear tests of steel plates to phenol-resin-impregnated glass-cloth honeycomb core (ref. 7) a strength of 320 psi was obtained at 400° F and 160 psi, at 600° F.

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TABLE 1.- EFFECT OF POSTCURE ON JOINT STRENGTH OF 0.064-INCH CLAD ALUMINUM-ALLOY LAP-SHEAR SPECIMENS BONDED WITH FPL-710 ADHESIVE

Initial cure		Postcure		Shear strength at 600° F, psi	
Time, min	Temperature, °F	Time, hr	Temperature, °F	Average	Minimum-maximum
30	320	None		470	80-1,160
30	320	3	450	840	540-1,290
30	320	192	450	1,248	1,100-1,488

TABLE 2.- TYPICAL AVERAGE TEST RESULTS OF LAP-SHEAR SPECIMENS BONDED WITH FPL-710 ADHESIVE APPLIED BY BRUSH, SPRAY, OR IMPREGNATED GLASS MAT

Application	Postcure		Average shear strength, psi, at test temperature of -			
	Time, hr	Temperature, °F	-70° F	80° F	450° F	600° F (a)
Brush	None	---	1,791	2,776	1,634	470(80-1,160)
Brush	192	450	1,852	1,740	1,852	1,248(1,100-1,488)
Spray	None	---	2,480	2,458	1,602	564(75-820)
Spray	192	450	------	1,810	-----	1,634(1,630-1,640)
Impregnated mat	None	---	1,664	2,692	1,607	900(610-1,160)
Impregnated mat	192	450	1,366	1,497	1,328	1,074(990-1,140)

[a]Numbers in parentheses give range of strength values for individual specimens.

TABLE 3.- SHEAR STRENGTH OF TITANIUM AND STAINLESS-STEEL LAP JOINTS COMPARED WITH THAT OF ALUMINUM-ALLOY JOINTS

Metal	Metal thickness, in.	Heat-exposure conditions,		Shear strength, psi, at test temperature of -		
		Time, hr	Temperature, °F	-70° F	80° F	600° F
Titanium RC-30	0.032	None	---	980	2,020	
		192	550	-----	48	---
Stainless steel, type 302	.016	None	---	2,540	2,680	430
		192	550	-----	1,490	---
Aluminum 24S-T3	.064	None	---	1,791	2,776	470
		192	550	-----	670	---